



PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
PATENT EXAMINING OPERATION

Applicant(s): Alan C. Cooper et al.

Serial No: 10/724,848

Group Art Unit: 1754

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Examiner: Stadler, R.

Docket No.: 06489 USA

Confirmation No.: 2180

For: Hydrogen Storage Via Adsorption Of Hydrogen On Small-Diameter, Chiral
Singlewalled Carbon Nanotubes

DECLARATION UNDER 37 CFR 1.131

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

I, Alan C. Cooper, am one of the inventors of the above-identified patent application, hereby declare that:

1. I am familiar with the Final Office Action mailed on July 10, 2006 and the cited article, Sudan et al., "Physisorption of hydrogen in single-walled carbon nanotubes", Carbon Volume 41, Issue 12, 2003, Pages 2377-2383 ("Sudan reference"). The publication date of the Sudan reference is 03 September 2003 which is less than one year before the filing date of this patent application which is 01 December 2003.

2. The conception of the invention claimed in the above-identified application occurred within the United States of America and prior to 03 September 2003. Evidence of such conception is provided in the form of copies of certain pages from my research notebook that are attached hereto as Exhibit A. These notebook pages were signed and witnessed before 03 September 2003. The dates from the notebook pages have been redacted.

3. This invention claimed in this patent application was conceived prior to 03

September 2003 and diligently reduced to practice.

4. I along with the other inventors were in possession of the claimed invention before 03 September 2003 and, therefore, the Sudan reference is not available as prior art to the claimed invention.

I further declare that all statements made herein of my own knowledge are true, and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine and/or imprisonment under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing therefrom.

Date: 25 October 2006

Alan C. Cooper
Alan C. Cooper

Attachment: Exhibit A – Redacted Notebook Pages



L0017097

EXHIBIT A

Micafilmed Complete

**AIR
PRODUCTS** 

RESEARCH & DEVELOPMENT NOTEBOOK No. 17097

USER'S NAME Alan C. Cooper

DEPARTMENT CSTC

LOCATION RD3 / C166

USED FRC... .., TO

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The standard volumetric apparatus (17097-18) was used to measure the hydrogen adsorption of pristine single wall carbon nanotubes (17097-20).

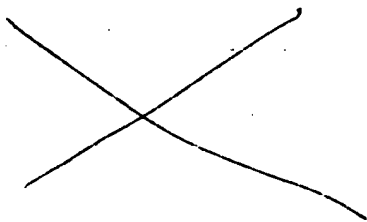
Volumetric Hydrogen Adsorption Determination

Temperature (K): 77
 Adsorbant: SWNT (formula C20 for comparison purposes)
 Molecular Weight: 240.22
 Reference volume (cm3): 1018.2
 Total volume (cm3): 1463.7
 He dead volume @ 77K and 800 torr expansion (cm3): 536.7
 He dead volume @ 298K and 800 torr expansion (cm3): 556.3
 Sample weight (mg): 500
 Sample (mmol): 2.081425

P1 (torr)	Time zero (torr)	10 sec. (torr)	30 sec. (torr)	60 sec. (torr)	2 min. (torr)	3 min. (torr)	Final (torr)	Calc.RTP (torr)
800	536.3	531.1	525.2	523.8	523.4	523.4	523.4	556.3

Calc.LNP (torr)	delta P (torr)	H2 ads. (mmol)	H2 ads. (mmol/g)	H2/Ads.	Wt. %
536.7	13.3	4.05405	8.108099	1.947728	1.62162

The results show that the pristine SWNT material has a higher H₂ capacity than the two potassium doped SWNT samples (17097-39A & B). This is very different than the case for pristine graphite vs. potassium doped graphite intercalation complexes of second stage and higher stages. Pristine graphite has essentially no H₂ adsorption while KCl₂₄ has fairly high capacity.



J. L. Van

Alan C. Cooper

A sample of SWNT from a CVD growth process () which was purified according to the process outlined in 17097-89 was placed in a quartz tube for volumetric H_2 adsorption measurements on the ASAP unit in the sorption characterization laboratory (RD1). The sample was initially degassed by heating to $550^\circ C$ for 16 hours. Upon cooling to room temperature, the sample was exposed to 470 torr H_2 . A very small pressure drop was noted (1.5 torr in a total volume of ca. 45 cc, sample size is 400 mg). The sample was cooled to 130 K and the head space evacuated for 15 minutes. Upon warming, a pressure rise of 2.5 torr (45 cc volume) was recorded between 150 - 450 K. Upon further heating, the H_2 pressure was observed to decrease slightly - the sample appears to remove gaseous H_2 either by reaction or adsorption. To probe this unusual high-temperature H_2 uptake, the sample was re-activated ($550^\circ C$, 16 h) and dosed with 510 torr H_2 at $400^\circ C$. A very rapid drop in the initial H_2 pressure was noted and this decrease was constant for a period of 2 hours. The sample was cooled, under H_2 , to $-78^\circ C$ and the head space evacuated (10 min.). Upon warming under a static vacuum, the pressure increased to ca. 2 torr at room temperature. Warming above R.T. resulted in more desorption, yielding a final pressure of 10 torr (45 cc total volume, 400 mg) at 675 K. At this temperature, the adsorbed H_2 and gaseous H_2 may be in equilibrium: removal of some H_2 from the gas phase caused additional desorption from the sample and a new equilibrium pressure was recorded. It is very important to note that no mass spec. is available for this expt. It may be possible, even likely, that the recorded pressure rise is due partially to gas evolution of species other than H_2 .

Jim L. Vait

Alan C. Cooper

In a number of experiments were conducted in the adsorption characterization laboratory (CRSD) on the h.p. microbalance. A sample of solution-purified SWNT (17097-86) was placed in the microbalance and activated by heating to 750°C under vacuum. A substantial amount of water, CO_2 , CO was evolved from the sample upon initial activation and it took nearly a week for a high vacuum to be achieved in the micro balance. No hydrogen adsorption was noted upon exposure of H_2 to the sample at room temperature. In an effort to further activate (or 'clean up') the sample, the sample was heated to 500°C under a static atmosphere of H_2 . After cooling the sample and evacuating the hydrogen the sample was re-activated under vacuum. The mass spectrometer detected a desorption of hydrogen upon warming. The evolution of H_2 from the sample continued until ca. 350°C .

In a series of experiments from hydrogen was exposed to the sample at temperatures ranging from $150 - 750^{\circ}\text{C}$. The sample was then cooled to ambient or lower temperature while the balance was evacuated. The sample was then heated under a dynamic vacuum with a mass spectrometer analyzing the gases evolving from the sample (TPD model). In all cases, H_2 was observed to desorb from the sample to temperature of $500 - 600\text{ K}$. CO is also observed at these temperatures. As the temp. rises above 900 K , H_2 and CO are observed to increase again, possibly due to oxidation of the carbon by background H_2O in the micro balance.

It is unusual to see that H_2 desorption occurs only after heating this sample under a hydrogen atmosphere. It may be possible that some sort of chemisorption (vs. physisorption) is occurring, with assistance of metal impurities in the sample.

Jim L. Van

Alan C. Cooper